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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE January 1994		3. REPORT TYPE AND DATES COVERED Interim	
4. TITLE AND SUBTITLE Charging Hydrogen into Ni in Hydride-Containing Molten Salts				5. FUNDING NUMBERS Contract No. N00014-92-J-1673	
6. AUTHOR(S) Bor Yann LIAW and Yi DING				R&T Code 413z004srp01	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Hawaii Natural Energy Institute University of Hawaii at Manoa 2540 Dole Street, Holmes Hall 246 Honolulu, HI 96822				8. PERFORMING ORGANIZATION REPORT NUMBER ONR Technical Report # 04	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 North Quincy St. Arlington, VA 22217				10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION/AVAILABILITY STATEMENT Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.				12b. DISTRIBUTION CODE	
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14. SUBJECT TERMS excess heat, molten salt techniques					
15. NUMBER OF PAGES 10				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED		18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED		19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	
20. LIMITATION OF ABSTRACT UNLIMITED					

94-23316



DTIC QUALITY INSPECTED 8

94 7 22 170

OFFICE OF NAVAL RESEARCH

GRANT: N00014-92-J-1673

R&T Code: 413z004srp01

Technical Report No. 04

Accession For	
NTIS	CRS
DTIC	12
Unannounced	12
Justification	
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Availability Codes	
Dist	Avail and/or Special
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by

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Prepared for Publication

in the

Proceedings of the 4th International Conference on Cold Fusion (ICCF-4)  
December 6-9, 1993, Lahaina, Hawaii

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January, 1994

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## CHARGING HYDROGEN INTO Ni IN HYDRIDE-CONTAINING MOLTEN SALTS

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### Abstract

Elevated-temperature calorimetric measurements were performed using a cell: Al 6061 alloy | LiH(saturated), LiCl-KCl eutectic | Ni with a charging current of about 600 mA. An anomalous positive temperature excursion was observed, which was difficult to explain based on our understanding of the electrochemical reactions occurring in the cell and the associated enthalpies. The potential between the working and counter electrodes fell in two peculiar ranges: in the initial stage, 0.7–1.2 V, and in a later stage, 2.3–2.6 V — a range of great interest — due to its similarity to the condition of an excess heat event that we reported in the Pd-D system in which significant excess heat was measured.

### Introduction

Excess power and heat accompanied with nuclear products have been measured in many recent experiments (1-12) using a variety of techniques to enhance deuterium or hydrogen absorption into metal matrices. Originally proposed by Fleischmann and Pons (13) was the electrolysis of heavy water with Pd cathode and Pt anode, in which reproducible "boiled-off" episodes and significant amount of excess heat of the order of over 200 eV per Pd atom were recently demonstrated (14). They have attributed this phenomenon to some unknown nuclear processes yet to be identified. Mills and his co-workers (15) independently reported excess heat using light water electrolysis with Ni cathode and Pt anode in potassium carbonate solutions. Mills and his co-workers (16,17) further proposed a theory attributing the excess heat to be originated from sub-ground-state energy levels of hydrogen. Similar excess heat results using light-water electrolysis have been reported by several other laboratories, including Bush (1) who proposed an "alkali-hydrogen fusion" model to claim his team's finding of enriched nuclear transformation. The origin of both excess heat phenomena are still an open question.

These reports, although difficult to explain, draw our interest to verify excess heat generation in Ni anode using hydride-based melt. This paper reports an instance in which apparent excess power was measured. Two previous experiments using a similar cell configuration but at different charging currents, 350 and 400 mA, also

exhibited anomalous temperature excursions at different magnitudes. The origin of this excess power was not clear, nor was the detail of reactions involved in the electrolysis. This preliminary experiment was not intended to detect any nuclear products, nor will any nuclear aspects be discussed. From thermodynamic point of view, it is very difficult to explain the thermal behavior exhibited by the cell.

### Experimental Aspects

The cell configuration was similar to what we previously reported. Figure 1 shows the schematic of this particular experimental setup. Ni electrode was made of a Ni thin-wall tubing obtained from Small Parts, Inc., Florida. The Al alloy electrode was a typical commercial 6061 tubing with a wall thickness of 1/8". Two thermocouples were used: One is an E-type (chromel-constantan couple) and the other is a K-type (chromel-alumel couple) probe, both made by Omega Engineering, Inc. Each probe was protected with a thin-wall ungrounded 304 stainless steel sheath and connected to an ice-point junction compensator to obtain correct temperature readings. Although the E-type probe is more sensitive to small temperature change than the K-type, both probes behaved consistently during the experiment. The K-type probe was placed inside the cathode holder, which was made of brass, about half an inch above the melt surface. The E-type probe was placed in the melt approximately half way between the cathode and the anode. A relatively constant temperature difference of about 10°C between the two probes was found throughout the experiment, almost independent of any electrolysis process.

The charging process was conducted under a galvanostatic mode with a constant current of 600 mA. We used a PARC 173 galvanostat for the electrolysis. Cell potential and temperature readings were collected by a data acquisition board and controlled by a Macintosh program written in LabVIEW. The board has a 16-bit resolution, which allows up to  $\pm 10$  V input and a gain of 100 to give the temperature reading a precision of about 0.035°C. We also intermittently monitored the cell current and the voltage and current of the furnace dc power supply through external digital multimeters to assure a constant cell current and furnace power input during the electrolysis. The dc furnace input power has been controlled at  $24.1 \pm 0.1$  W throughout the experiment, therefore the possible drift in the cell temperature was about  $\pm 1^\circ\text{C}$ . The calorimeter was calibrated at the end of the run by varying the furnace power in a step fashion and recording the steady temperature variation at intervals of at least 6 hours. A linear calibration curve from each temperature probe was shown in Figure 2 with a cell constant of about  $10.3^\circ\text{C W}^{-1}$ .

### Results and Discussions

Figure 3 displays the temperature variations measured by the two probes and the cell potential excursion during the run. There are several interesting features from this result:

1. The cell potential exhibits two distinct ranges: one begins at about 0.7 V and rises to about 1.2 V gradually in three disparate intervals (named as the first charging stage), and another fluctuates between 2.3 V and 2.6 V and sometimes exceeds 3 V in two intervals (named as the second charging stage) during the electrolysis. The two distinct potential ranges indicate that the cell has been operated under two different reactions (stages). The one between 0.7 and 1.2 V is considered to be associated with hydrogen evolution, according to our recent cyclic voltammetry results (18). The overpotential increase with time is likely due to the decreasing LiH content in the melt. There is a possibility of a two-electron hydride-to-proton charge transfer reaction involved at this stage, which may lead to a "shuttle mechanism" that results in a prolonged anodic charging process and loss in Coulombic efficiency. The potential range between 2.3 and 2.6 V is presumably due to nickel or iron chloride formation, which corrodes the Ni metal electrode or the steel lead. According to the values in Table 1, the potential for both reactions are very similar. The fluctuation between two potential ranges was often observed in the molten salt electrolysis, but the mechanism is not characterized at this time. This fluctuation makes the interpretation of the calorimetric results complicated.
2. The temperature probes show different sensitivity of thermal response toward electrode reactions. The E-type probe in the melt was more sensitive to potential excursions than the K-type probe in the cathode holder, as shown in Figure 3. This difference was probably due to a combination of
  - a less effective heat transfer in the melt/anode region than in the metal holder/cathode region, resulting in a larger temperature excursion in the vicinity of the anode and indicating some degree of local heating, and
  - a closer proximity of the E-type probe to the anode than the K-type probe.This difference causes some precautions to our interpretation of the calorimetry data. However, the results from the K-type probe should give us a lower-bound of the overall thermal behavior, despite that some characteristics of the potential excursion was sacrificed. In this way we will underestimate the excess heat in the cell. On the other hand, the location of the probe still influences the detection of thermal behavior, which is a cause for concern. Nonetheless, the consistency of the two probes in reflecting the relative change of power, as described below, indicates that the thermal response measured by both probes is independent of the probe location.
3. The temperature probes show a consistent baseline temperature rise during the electrolysis. Despite the different response to the potential excursion, the two probes consistently reflect a steady increase of baseline temperature in their respective temperature profiles, suggesting that there may be a heat source in the cell induced by the anodic charging process.

Unfortunately, the cell failed after about 3.4 hours of operation, prohibiting a final temperature plateau, if any, to be measured. There was a scattered thermal response region for E-type probe after 3 hours of operation, and the reason is not clear. The cell potential was very unstable at that time, signifying the working electrode was not functioning properly and eventually resulted in a cell failure, destroyed the A/D

board and the E-type probe. The working electrode lead was found broken when the cell was disassembled.

Figure 4 shows the input and output power profiles of the experiment. The input electrochemical power is the product of the current and cell potential. The output power measured from both probes are interpreted from the post-calibration curves shown in Figure 2. The two output curves are similar except for the regions of high potential excursion. Excess power was observed in both probes after about 1.7 hours of operation. However, because the input power decreased from 1.5 W to 0.5 W at that time, the interpretation of excess power was obscured between 1.7 and 2.4 hours. After 2.4 hours, the excess power over the large 1.5 W input power was apparent. At 2.9 hours the excess power was about 0.5 W over the 1.5 W input, or about 33%. It should be noted that the scattering of the thermal response in the curves shows the overall noise level of the temperature and power measurements, which is significantly lower than the magnitudes of the temperature rise and excess power measured in the experiment; therefore, random errors can not explain the excess power result.

In summary, the K-type probe in the cathode holder gave a more conservative and less potential-dependent measurement of the cell thermal behavior during the anodic charging process. A consistent yet "unknown" heat source caused a temperature rise in the cell and resulted in excess power measured of the order of 0.5 W over the input power of 1.5 W. This phenomenon cannot be explained by random error in the measurement nor any storage mechanism.

A more detailed heat balance and estimation of the anomalous thermal behavior of the cell can be obtained by examining the electrochemical reactions involved in the electrolysis. The enthalpy of these reactions can be used for comparison with the calorimetry data. The possible reactions under consideration are listed in Table 1. During the initial electrolysis the half-cell reactions are:

Dissociation of LiH in the electrolyte:



$\beta$ -LiAl formation at the cathode:



Hydrogen evolution at the anode:



and the total cell reaction is:



The enthalpy of the total reaction [4] is endothermic. Accordingly, there should be a power decrease of 0.26 W at 600 mA from this reaction. The initial power input of this reaction was about 0.42 W (0.6 A  $\times$  0.7 V) and gradually increased to 0.72 W (0.6 A  $\times$  1.2 V). The difference between the input power and the power consumption from the endothermic reaction enthalpy will be treated as total IR loss that turned into waste heat, which should be about 0.16 W initially and increase to 0.46 W eventually. This waste heat should raise the cell temperature only by 1.6°C to 4.6°C, respectively, in contrast to the measured baseline temperature rise of about 20°C at 3.2 hours. The cell temperature rise was about an order of magnitude larger than what we expected from this reaction.

Another possibility of heat release could come from the two-electron charge-transfer hydride-to-proton reaction and speculated "shuttle mechanism" possibly involved at the end of the first charging stage according to:



The substantial positive enthalpy will reduce the input power by 1.02 W, which will adversely decrease the cell temperature by 3–6°C. Even if the reaction also occurred at the second stage with a high input power of 1.56 W (0.6 A  $\times$  2.6 V), the IR-loss heat rate is still only about 0.54 W or contributes to only 5.4°C increase. The measured excess power value is much larger than what we expected from this effect.

We further consider the heat balance in the second charging stage in which metal chloride formations, such as [11] and [12] in Table 1, occur. The enthalpies for NiCl<sub>2</sub> and FeCl<sub>2</sub> formations are 97.97 and 89.61 kcal mol<sup>-1</sup>, respectively. These reactions will subtract the input power by 1.27 and 1.17 W, respectively. With the associated input power of 1.56 W (0.6 A  $\times$  2.6 V), we found the IR-loss heat rate only accounts for 0.29–0.39 W or 2.9–3.9°C in cell temperature rise, still considerably less than what was measured. Besides, the excess power seems to occur from the beginning of the electrolysis, in which the chloride reaction should not involve.

More recently, we have conducted some electrolysis experiments using steel leads as the anode. The results, which will be discussed elsewhere, showed no excess power even though the cell potential reached above 2.2 V, a distinct range of interest for the second charging stage and as a contrast to the Ni-based experiments. We can treat the steel-based system as blank or control experiments. The result indicates that the excess power seems to be associated with the presence of Ni. In the future, we need to distinguish the Ni-based system that produces excess power from the one that doesn't. We should also characterize the parameters that cause the difference.

It should be cautioned, however, that although the excess power and temperature excursions were significantly greater than the values expected from the enthalpy of reactions and the IR-loss heat, the magnitude of the excess power (~0.5 W) is still small compared to the dc power to the external furnace (24.1 $\pm$ 0.1 W).

## Conclusion

We found a relatively consistent anomalous thermal excursion in the electrolysis of an Al 6061 alloy | LiH(saturated), LiCl-KCl eutectic | Ni cell. The temperature increase was significantly larger than what we would expect from various possible reaction enthalpies. The cell potential exhibited a similar pattern to what we have measured in previous Pd-D experiments. The consistent behavior reflected by different probes indicates that the anomalous thermal excursion seems to be real and not attributed to any systematic error or storage process.

## Acknowledgments

This work was supported in part by the U.S Office of Naval Research and by the Office of Technology Transfer and Economic Development in the University of Hawaii.

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Table 1. Enthalpy and Free Energy of Reactions Involved in the Electrolysis at 700 K.  
(1 kcal = 4.186 kJ)

Reaction	$\Delta G^\circ$ , kcal mol <sup>-1</sup>	$\Delta H^\circ$ , kcal mol <sup>-1</sup>	$\mathcal{E}^\circ$ , V	Ref.
[5] $\text{LiH} = \text{Li} + \frac{1}{2} \text{H}_2$	8.53	22.64	0.370	$\text{Li}^+/\text{Li}$
[6] $\text{Li} + \text{Al} = \beta\text{-LiAl}$	-6.85	-12.72	0.297	$\text{Al}/\beta\text{-LiAl}$
[7] $\text{LiH} + \text{Al} = \beta\text{-LiAl} + \frac{1}{2} \text{H}_2$	1.68	9.92	0.073	$\text{Al}/\beta\text{-LiAl}$
[8] $\text{LiCl} = \text{Li} + \frac{1}{2} \text{Cl}_2$	83.87	97.66	3.637	$\text{Li}^+/\text{Li}$
[9] $\frac{1}{2} \text{H}_2 + \frac{1}{2} \text{Cl}_2 = \text{HCl}$	-23.60	-22.36	1.023	$\text{H}^+/\text{H}_2$
[10] $\text{LiH} + \text{LiCl} + 2 \text{Al} =$ $2 \beta\text{-LiAl} + \text{HCl}$	55.10	78.10	1.195	$\text{Al}/\beta\text{-LiAl}$
[11] $2 \text{LiCl} + 2 \text{Al} + \text{Ni} =$ $2 \beta\text{-LiAl} + \text{NiCl}_2$	106.46	97.97	2.308	$\text{Al}/\beta\text{-LiAl}$
[12] $2 \text{LiCl} + 2 \text{Al} + \text{Fe} =$ $2 \beta\text{-LiAl} + \text{FeCl}_2$	93.24	89.61	2.022	$\text{Al}/\beta\text{-LiAl}$

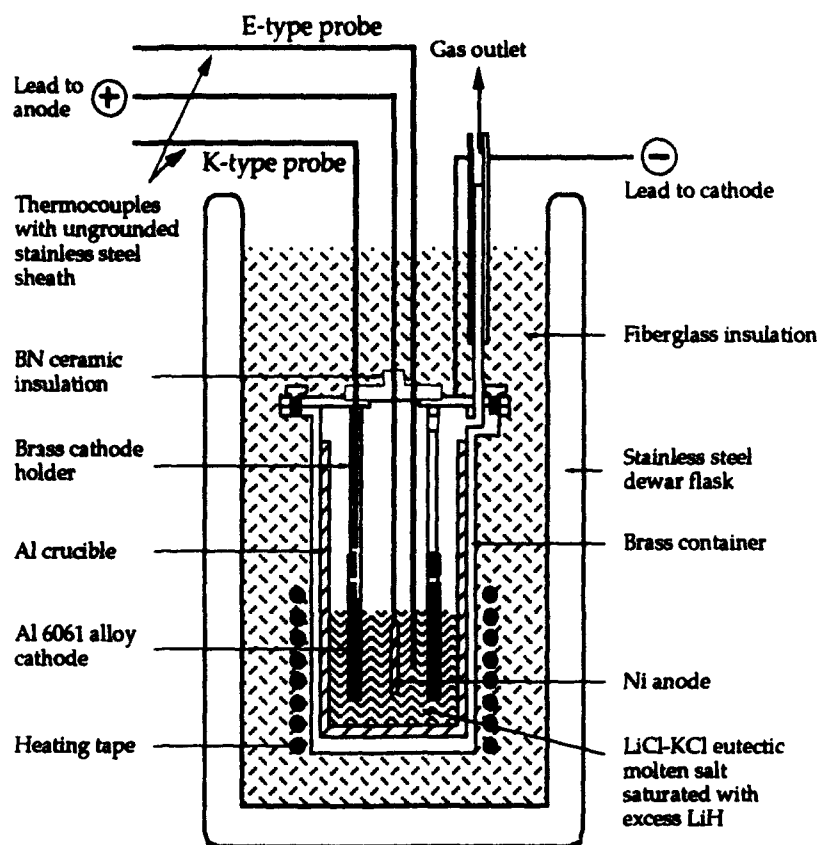


Figure 1. Schematic of the molten salt cell.

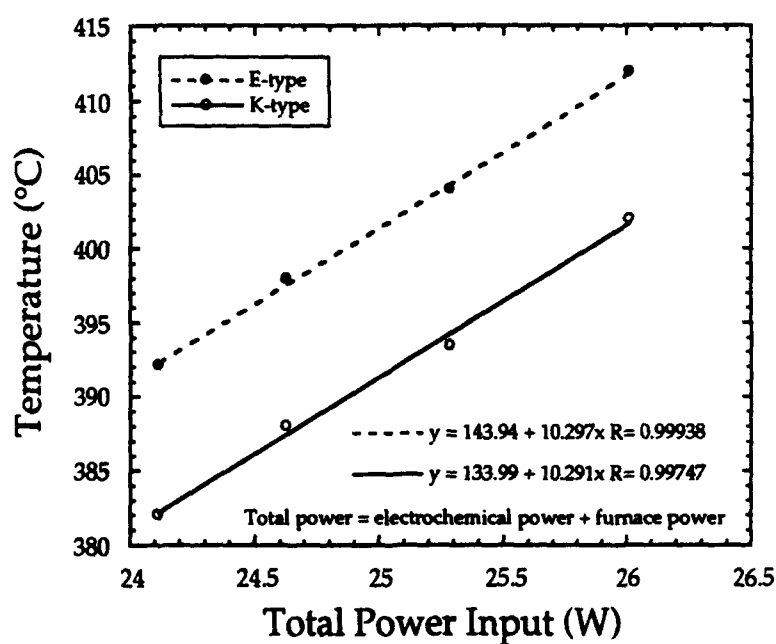


Figure 2. Post calibration curves of the experiment with a cell constant of  $10.3^{\circ}\text{C W}^{-1}$ .

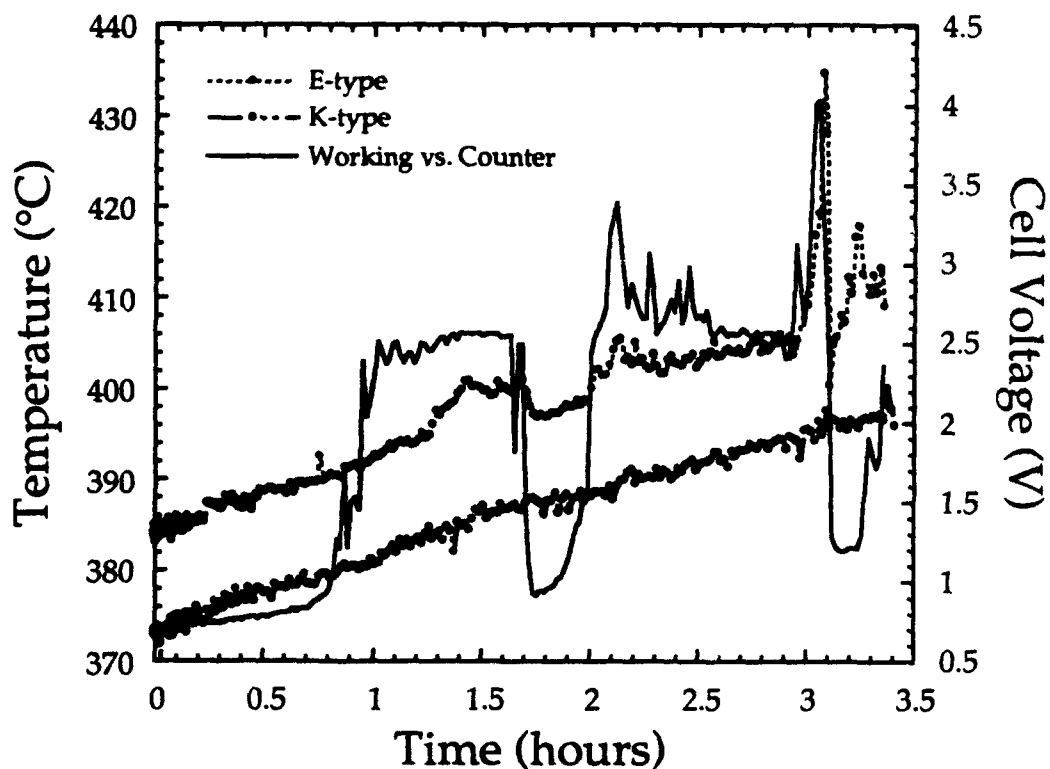


Figure 3. Temperature profiles and cell voltage during the electrolysis.

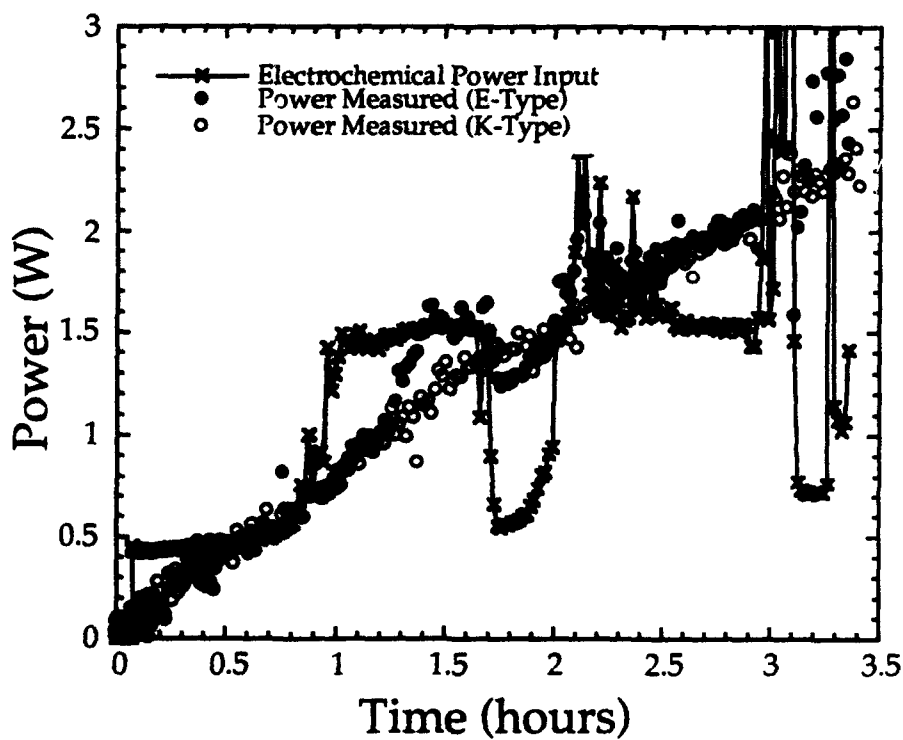


Figure 4. Input and output power profiles during the electrolysis.